

# PATENT SPECIFICATION

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## (54) PROCESS FOR AZEOTROPIC DISTILLATION

(71) We, MITSUI PETRO-CHEMICAL INDUSTRIES, LTD., a Japanese Company of 2-5, Kasumigaseki 3-chome, Chiyoda-ku, Tokyo, Japan, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

10 This invention relates to a process for separating a compound from water in a mixture of the compound and water by azeotropic distillation in the presence of an entrainer.

15 Heretofore, separation of for example acetic acid from water in the mixture has been effected by azeotropic distillation in the presence of an entrainer, that is, the azeotropic mixture of water and the entrainer is distilled from the top of a fractionating column while dehydrated acetic acid or a concentrated acetic acid is withdrawn from the bottom. This method is disclosed in U.S. Patent Nos. 1,917,391 and 2,050,234 and British Patent No. 298,137. This azeotropic distillation has various advantages such as a high efficiency of separation, low reflux ratio and a reduced heat energy required for distillation.

30 However, according to this azeotropic distillation, the gas-liquid composition distribution in the column is much more complicated than that in a usual distillation, and such distribution is easily changed even by a slight change in quantity, composition, and temperature of the feed, quantity of refluxed entrainer, reflux ratio of the aqueous phase and other operating conditions and therefor, a stable operation of a distillation column is very difficult. For example, a minor change in the operating conditions results in adversely affecting the separation efficiency at the top of the column and contamination of a bottom product with the entrainer when a higher boiling entrainer is used. In a usual distillation, when such change in a gas-liquid composition distribution in a distillation column occurs, a stable

operation can be carried out by controlling the operation conditions such as reflux ratio, heat energy supplied to a reboiler and the like. However, in case of azeotropic distillation, simple control of the quantity of reflux of the entrainer and heat supply to the reboiler are not sufficient to suppress a change in the gas-liquid composition distribution in the distillation column, in particular a change in the azeotropic zone, further in particular, a change in the lower region of said azeotropic zone where the content of the entrainer in the liquid composition varies to a great extent.

The present invention provides a process for separating a compound from a mixture of the compound with water by azeotropic reflux distillation while feeding an entrainer to the mixture, which process comprises monitoring the temperature at a particular position in the lower region of an azeotropic zone to which lower region entrainer is fed, and varying the rate of feed of the entrainer to the said lower region of the azeotropic zone in response to detected temperature changes to maintain the temperature at said position substantially constant and hence maintain a substantially constant composition distribution in the azeotropic zone.

Using the process of the present invention it is possible to suppress changes in composition distribution in the azeotropic zone. In this way, the azeotropic distillation is stabilized and neither the distillate product nor the bottom product is contaminated with the entrainer. The distillation column can be operated steadily under a low reflux ratio.

In conventional processes particularly in the lower region of the azeotropic zone the content of the entrainer in the liquid composition varies to a great extent.

A preferred embodiment of the present invention will be described hereinafter with reference to the accompanying drawings wherein:

Fig. 1 shows schematically distillation apparatus which may be used for azeotropic

distillation according to the present invention;

Fig. 2A shows a liquid composition distribution in a distillation column where separation of acetic acid and water is conducted by an azeotropic distillation using butyl acetate as an entrainer; and

Fig. 2B shows a temperature distribution in a distillation column as mentioned above.

According to the present invention, the composition of the components, namely water and another compound, fed to a distillation column is optional.

For example, when the compound is acetic acid, a mixture of acetic acid and water which contains 10—95% by weight of water, preferably, 40—95% by weight of water, may be used.

As an entrainer, there may be employed various compounds which have been, heretofore, used as entrainers for azeotropic distillation for a mixture of water and acetic acid. Representative entrainers are esters such as butyl formate, amyl formate, isoamyl formate, allyl acetate, butyl acetate, n-propyl propionate, isopropyl propionate, allyl propionate, butyl propionate, isobutyl propionate, methyl butyrate, ethyl butyrate, propyl butyrate and isopropyl butyrate; ethers such as dichloromethyl ether, ethyl isoamyl ether, allyl isoamyl ether, ethyl amyl ether, di-n-butyl ether and di-isobutyl ether; halogenated hydrocarbons such as amyl chloride, ethylene dichloride, propylene dichloride and chlorobenzene; ketones such as chloroacetone, ethyl propyl ketone, dipropyl ketone, methyl butyl ketone, methyl isobutyl ketone, allyl acetone and mesityl oxide; aromatic hydrocarbons such as toluene, xylene and ethyl benzene and other similar compounds having a boiling point of from 100° to 150°C and capable of forming an azeotropic mixture with water. Among these entrainers, esters having a boiling point of 100 to 150°C are preferable and in particular, butyl acetate.

Other than the above mentioned distillation involving a heterogeneous azeotropic system for a mixture of water and acetic acid where the azeotropic mixture forms two liquid phases of different composition, there may be mentioned the following heterogeneous azeotropic distillations:

n-butanol-water system where the entrainer may be hexane, cyclohexane, heptane, octane or nonane;

ethanol-water system where the entrainer may be  $\text{CS}_2$ ,  $\text{CCl}_4$ , bromoethane or benzene; propanol-water system where the entrainer may be  $\text{CCl}_4$ , tetrachloroethylene, benzene, toluene or hexane;

methanol-water system where the entrainer may be  $\text{CS}_2$ , benzene or toluene.

The azeotropic distillation can be carried out under atmospheric pressure, elevated pressure or reduced pressure, but usually it is carried out under atmospheric pressure. The azeotropic distillation can be effected either batchwise or continuously.

According to a preferred embodiment of the present invention, for example, in case of acetic acid-water system, an azeotropic mixture of water and an entrainer is distilled from the top of the column and when the azeotropic mixture is cooled, it is separated into two phases, an aqueous phase and an entrainer phase. One part of the aqueous phase is refluxed to the top of the column, if necessary, and the other part is withdrawn while the entrainer phase is refluxed to the top of the column and to the lower region of the azeotropic zone in the column. From the bottom of the column, dehydrated acetic acid or a concentrated acetic acid is obtained.

The quantity of the entrainer to be refluxed to the top of the column depends upon the composition of the mixture of water and acetic acid, the theoretical plate number of the column, type of entrainer, and the operating conditions.

Where an azeotropic distillation of acetic acid and water is effected in the presence of an entrainer according to the present invention, the liquid composition distribution and the temperature distribution in a distillation column are as shown in Figs. 2A and 2B.

Fig. 2A shows a liquid composition distribution in a distillation column where a mixture of 43.49% by weight of acetic acid and 56.51% by weight of water is subjected to an azeotropic distillation in the presence of butyl acetate as an entrainer using a distillation column having 50 plates at a molar reflux ratio of 0.65 and Fig. 2B shows a temperature distribution in the distillation column.

The term, "azeotropic zone" used herein means a region in a distillation column where the concentration of an entrainer in a liquid composition is 0.1% by weight or more. For example, the region between A and C in Figs. 2A and 2B is an azeotropic zone. At the upper region of this azeotropic zone (between A and B in Figs. 2A and 2B), variation of content of the entrainer in the liquid composition is little except at the upper-most plate while at the lower region of the azeotropic zone (between B and C in Fig. 2), the variation of the content of the entrainer is large and, thereby, variation of temperature at that part of the column is also large. In such azeotropic distillation, vapor-liquid composition distribution in the azeotropic zone, particularly that at the lower region of the azeotropic zone, is changed to a great extent by even a small

change of operating conditions such as composition, quantity and temperature of a feed charged to a distillation column, quantity of reflux of the entrainer and quantity of heat supplied to a reboiler. As a result, the distillation can not be carried out under steady conditions. For example, the region of the azeotropic zone between B and C tends to move upwards or downwards and therefore, the entrainer contaminates the concentrated acetic acid in the bottom product while the separation efficiency of water from acetic acid is lowered at the top of the column.

A large change of temperature is observed at any given position in the lower region of the azeotropic zone when the gas-liquid composition changes at that position and therefore, it is possible to detect the change in composition in the azeotropic zone by measuring the temperature change. As a means for detecting the change in the azeotropic zone, the measurement of temperature change is used because it is simple.

A temperature controlling valve may be used for adjusting the reflux quantity of an entrainer and the quantity of an entrainer fed to the lower region of the azeotropic zone.

The quantity of an entrainer fed to the lower region of the azeotropic zone is varied in response to changes of temperature at the lower portion of the azeotropic zone, and the ratio of the quantity of an entrainer fed to the lower region to the quantity of the refluxing entrainer is usually in a range of from 0.01 to 0.50, preferably from 0.01 to 0.20.

The following examples are given for illustrating the present invention.

#### EXAMPLE

The process of the present invention was carried out using a continuous distillation apparatus as shown in Fig. 1. As an entrainer, butyl acetate was used and the fractionating column was a ripple tray type column having 50 plates.

At the beginning of the continuous azeotropic distillation, a mixture of 43.49% by weight of acetic acid and 56.51% by weight of water was fed to the column 1 having a reboiler 4 and the distillation was carried out under total reflux, and then butyl acetate was gradually fed to column 1 from a decanter 3 to form a ternary azeotropic system of acetic acid-water-butyl acetate. Then a mixture of 43.49% by weight of acetic acid and 56.51% by weight of water was fed through a feed inlet 5 positioned between the 21st plate and the 22nd plate at a rate of 178.52 Kg/hr. and concentrated acetic acid was withdrawn as a bottom product at a rate of 83.21 Kg/hr. from a

bottom outlet 6 while an aqueous phase in a decanter drum 3 connected to a cooler 2 was withdrawn through a water withdrawing line 7 at a rate of 95.32 Kg./hr. (D), and another portion of the aqueous phase (11.354 Kg./hr.) ( $R_w$ ) and an organic phase in decanter drum 3 (272.31 Kg./hr.) ( $R_o$ ) were returned to the top of column 1 as reflux to carry out the continuous azeotropic distillation. The flow rate of the organic phase (butyl acetate) as reflux was controlled by a flow rate controlling valve 8. Further, the temperature at the 31st plate of the column (in the lower region of the azeotropic zone as is clear from Fig. 2A and Fig. 2B) was detected and was adjusted to 94°C by feeding appropriately a part(s) of the organic phase (butyl acetate) in decanter drum 3 to a portion between the 26th plate and the 27th plate through a temperature-controlled valve 9. The feed quantity (S) of the organic phase (butyl acetate) at a stable continuous azeotropic distillation operation was 30.45 Kg./hr. and the ratio to the reflux organic phase ( $S/R_o$ ) was 0.1118. The reflux ratio (i.e. the ratio of the aqueous and organic phases refluxed to the amount of water withdrawn), ( $R_w+R_o+S$ )/D, was 0.65 (molar ratio). Fig. 2A shows the liquid composition distribution in column 1 when the continuous azeotropic distillation reached a constant state. In Fig. 2A, curve (I) denotes acetic acid, curve (II) water and curve (III) butyl acetate, and a temperature distribution in column 1 is shown in Fig. 2B.

This continuous distillation was effected for 9 hours. The temperature at the bottom of column 1 was  $114.5 \pm 0.1^\circ\text{C}$ , the temperature at the top of column 1 was  $90.5 \pm 0.1^\circ\text{C}$  and the temperature at the 31st plate in the lower region of the azeotropic zone was  $94.0 \pm 0.1^\circ\text{C}$ . These temperatures were very stable and the temperature distribution in column 1 hardly deviates from the temperature distribution curve in Fig. 2B. Content of acetic acid in the concentrated acetic acid withdrawn from the bottom of the column was steady at 93.30% by weight while that of water was steady at 6.70% by weight, and during the continuous distillation, butyl acetate was not detected at all. Content of acetic acid in the aqueous phase withdrawn from decanter drum 3 was steady at 0.007% by weight and that of butyl acetate was also steady at 0.50% by weight.

#### COMPARISON EXAMPLE

The operation of Example 1 was repeated except that none of the organic phase from decanter drum 3 was fed to the portion between the 26th plate and the 27th plate and therefore, the total quantity (302.76 Kg./hr.) of the organic phase was returned

to the top of column 2 as a reflux. As the distillation proceeded, the concentration of acetic acid in the aqueous phase in decanter drum 3 increased and amounted to 7.4% by weight, and the concentration of butyl acetate contained in acetic acid withdrawn from the bottom of column 1 was 0.01% by weight. This result shows that a stable azeotropic distillation can not be effected if none of the organic phase from decanter drum 3 is fed to the lower region of the azeotropic zone.

WHAT WE CLAIM IS:—

1. A process for separating a compound from a mixture of the compound with water by azeotropic reflux distillation while feeding an entrainer to the mixture, which process comprises monitoring the temperature at a particular position in the lower region of an azeotropic zone to which lower region entrainer is fed, and varying the rate of feed of the entrainer to the said lower region of the azeotropic zone in response to detected temperature changes to maintain the temperature at said position substantially constant and hence to maintain a substantially constant composition distribution in the azeotropic zone.

2. A process according to claim 1 wherein the said compound is acetic acid.

3. A process according to claim 2 wherein the entrainer is an ester having boiling point of from 100 to 150°C.

4. A process according to claim 3 wherein the ester is butyl acetate. 35

5. A process according to claim 1 wherein the said compound is n-butanol and the entrainer is selected from hexane, cyclohexane, heptane, octane and nonane. 40

6. A process according to claim 1 wherein the said compound is ethanol and the entrainer is selected from CS<sub>2</sub>, CCl<sub>4</sub>, bromoethane and benzene.

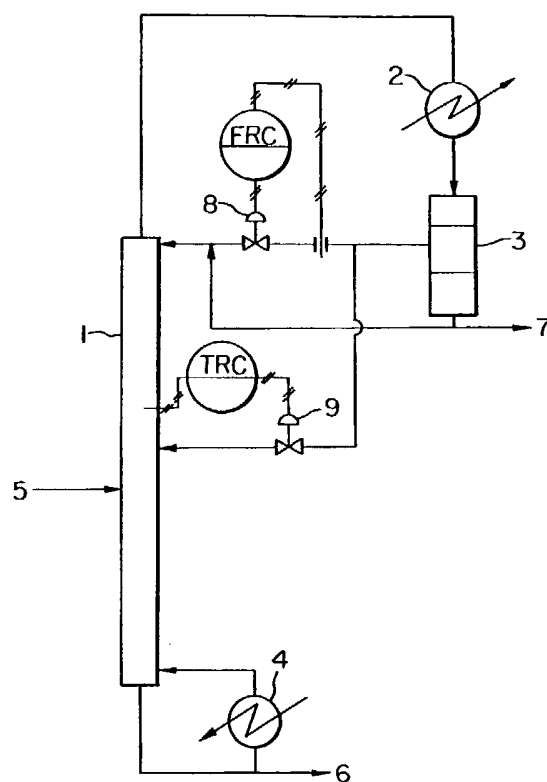
7. A process according to claim 1 wherein the said compound is propanol and the entrainer is selected from CCl<sub>4</sub>, tetrachloroethylene, benzene, toluene and hexane. 45

8. A process according to claim 1 wherein the said compound is methanol and the entrainer is selected from CS<sub>2</sub>, benzene and toluene. 50

9. A process according to claim 1 substantially as herein described and exemplified. 55

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FIG. 1



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COMPLETE SPECIFICATION

2 SHEETS

*This drawing is a reproduction of  
the Original on a reduced scale  
Sheet 2*

FIG. 2B

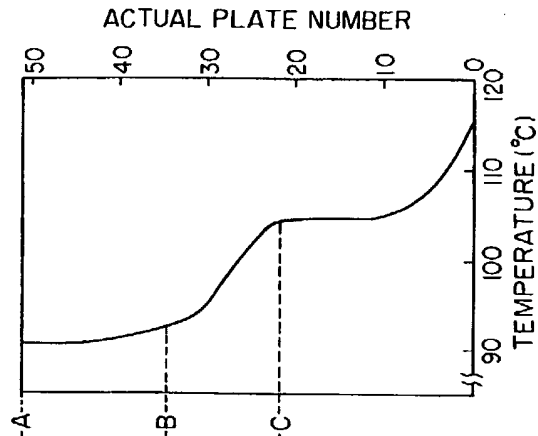


FIG. 2A

